



Using gelatin protein to facilitate paper thermoformability



Alexey Khakalo^a, Ilari Filpponen^{a,*}, Leena-Sisko Johansson^a, Alexey Vishtal^b, Arcot R. Lokanathan^a, Orlando J. Rojas^{a,c}, Janne Laine^a

^aAalto University School of Chemical Technology, Department of Forest Products Technology, P.O. Box 16300, 00076 Aalto, Finland

^bVTT Technical Research Centre of Finland, P.O. Box 1603, Koivurannantie 1, Jyväskylä 40101, Finland

^cNorth Carolina State University, Departments of Forest Biomaterials and Chemical and Biomolecular Engineering, Raleigh, NC 27695, USA

ARTICLE INFO

Article history:

Received 7 July 2014

Received in revised form 23 September 2014

Accepted 24 September 2014

Available online 2 October 2014

Keywords:

Cellulose modification

Gelatin

Paper formability

Paper extensibility

Packaging

ABSTRACT

One of the main challenges of fiber-based packaging materials is the relatively poor elongation of cellulose under stress, which limits formability and molding in related products. Therefore, in this investigation we first used cellulose thin films and surface sensitive tools such as quartz crystal microbalance (QCM-D), surface plasmon resonance (SPR) and X-ray photoelectron spectroscopy (XPS) to evaluate the cellulose–gelatin interactions. It was found that the highest adsorption of gelatin onto cellulose occurred at the isoelectric pH of the protein. Based on this and other results, a gelatin loading is proposed to facilitate molecular and surface interactions and, thus to improve the formability of cellulose-based materials in paper molding. Aqueous gelatin solutions were sprayed on the surface of wet webs composed of softwood fibers and the chemical and mechanical changes that occurred were quantified. Upon gelatin treatment the elongation and tensile strength of paper under unrestrained drying was increased by ~50% (from ~10% to 14%) and by ~30% (from 59 to 78 N m/g), respectively. The mechanical performance of gelatin-treated fibers was further improved by glutaraldehyde-assisted cross-linking. The proposed approach represents an inexpensive and facile method to improve the plasticity of fiber networks, which otherwise cannot be processed in the production of packaging materials by direct thermoforming.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Environmental concerns and a more reasonable use of fossil resources have amounted to a growing interest for renewable and biodegradable packaging materials [1]. Cellulose is one of the most abundant biopolymers in the biosphere and the main raw material in production of paper and board [2]. However, one of the main challenges of using cellulose-based packaging materials (such as cups, plates, trays and food containers) is the poor formability of cellulose [3]. Moreover, the barrier properties and moisture resistance of cellulose-based materials are not competitive when compared against traditional plastics. While barrier properties and moisture resistance can be improved by introducing additional coating layers, paperboard formability requires mechanical and chemical modifications of fibers and the fiber network structure to make it feasible.

The term “formability” describes the ability of a material to undergo plastic deformation without damage and it is an essential property for 3D-forming processes, where various advanced

shapes can be produced. As of today, the most stretchable bio-based composite materials have been prepared by reinforcing ductile hydrophobic matrices with natural fibers [4]. However, the interfacial adhesion between the components is not very good and chemical modification of natural fibers is typically required to improve the mechanical properties of such composites [5,6]. It is also important to note here that natural fibers are typically used to a lesser extent when compared to the hydrophobic component of the composites.

The main features of paper and paperboard for deep-drawing processes have been recently studied and the ability of a material to deform under applied stress without a failure has been highlighted [3]. The combination of high-consistency wing defibrator refining and subsequent low-consistency valley beating of fibers (laboratory process only) was proposed as a mechanical treatment to improve the extensibility and elongation at break without deteriorating the strength properties of resulting paperboard [7]. High-consistency treatment decreased the axial stiffness of fibers while the low-consistency refining improved fiber–fiber bonding by strengthening the fibers. It was also reported that the improved bonding between fibers promotes the stretch potential of curly fibers making the paper more extensible [8]. Furthermore, the

* Corresponding author. Tel.: +358 503605623.

E-mail address: erkko.filpponen@aalto.fi (I. Filpponen).

importance of paper drying was also acknowledged, i.e., the shrinkage of paper upon unrestrained drying (negative strain) could be further recovered to increase the overall extensibility of a paper.

The extensibility can also be improved by modifying the fiber or fiber network structure. For example, hydroxypropylation of cellulose was used to produce highly extensible and translucent paper [9]. Stretchable paper-based material has been prepared by converting a selectively dissolved fiber surface into the matrix [10,11]. Moreover, the elastic properties of a paper have been improved by applying film forming methylcellulose and lignosulfonate as surface sizing agents [12]. Approximately 50% increase in strain to failure was observed by employing a recombinant cellulose crosslinking protein [13]. Agar has also been used as an additive for improving the extensibility of paper [14]. In addition, the combination of gelatin and nanocellulose substrates has been shown to produce materials with excellent stress performance [15–17].

Gelatin is a mixture of proteins obtained by the hydrolysis of collagen, the most abundant protein in waste products like skins, connective tissues, bones and cartilage of predominant bovine animals. When heated to 40 °C, gelatin dissolves in water with a formation of random coiled chains. Upon cooling, gelatin chains partially recover the original triple-helix structure of collagen. Thus, gelatin gels form an ensemble of physically interconnected triple helices, which are held together by intermolecular hydrogen bonds. From the point of view of its chemical structure, gelatin is a weak polyampholyte. Typically, approximately 13% of gelatin backbone is positively charged (lysine and arginine), ~12% is negatively charged (glutamic and aspartic acid) and ~11% is hydrophobic in nature (leucine, isoleucine, methionine and valine) [18]. Gelatin is widely utilized in the food industry. In pharmaceutical field gelatin is used in controlled delivery systems [19,20] and for fabrication of three-dimensional gelatin-based polymer scaffolds for tissue-engineering and wound dressing purposes [21–23]. Moreover, gelatin-based films and interpenetrating polymeric networks have been proposed as alternatives to synthetic food packaging materials [2,16,24].

Apart from the aforementioned advantages of gelatin, there are some drawbacks that hinder its applications, among which poor mechanical properties and moisture sensitivity are the most limiting ones. Different approaches to overcome these drawbacks have been proposed but chemical cross-linking is by far the most effective method to improve mechanical, thermal, and water-resistance properties of gelatin. A variety of chemicals, biomolecules and enzymes have been used for cross-linking, such as glutaraldehyde [18,19], epoxides [25], glyoxal [26], isocyanates [27], formaldehyde [25,26], glycerinaldehyde [28], genipin [29] and transglutaminase [30]. However, glutaraldehyde is the most widely used due to its commercial availability, short-reaction time and low cost. In addition, it has an excellent ability to stabilize collagenous materials and therefore to improve the strength properties and water resistance [18].

Gelatin has been widely studied for its gel and film forming abilities in combination with cross-linker, like glutaraldehyde, or with plasticizer, like glycerol and sorbitol. However, despite the growing interest, to our knowledge there are no reports available on the application of gelatin for production of highly extensible paper and paperboard. In this communication, we first unveil the nature of cellulose–gelatin interactions by using quartz crystal microbalance with dissipation monitoring (QCM-D) and surface plasmon resonance (SPR) to then apply aqueous gelatin solution via spraying on cellulose fiber networks. As a result, an improved formability of paper was achieved. The morphology and composition of adsorbed gelatin layer were analyzed by scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray

photoelectron spectroscopy (XPS), all of which provide supporting evidence of the mechanism and mode of action of gelatin as an inexpensive and facile method to endow fiber networks with plasticity to make them suitable for 3D thermal forming.

2. Experimental

2.1. Materials

First thinning bleached softwood kraft fiber sheets (cellulose 81.7%, xylan 9.2%, glucomannan 9.0% and total lignin <0.5%) were provided by Pietarsaari mill, UPM-Kymmene. Gelatin from porcine skin (Type A, ~300 g Bloom gel strength, #232-554-6), glutaraldehyde solution (50 wt.% in H₂O, #340855) and polystyrene (280 kDa molecular weight, #182427) were obtained from Sigma–Aldrich (US). Trimethylsilyl cellulose (TMSC) was synthesized as described elsewhere [31].

2.2. Preparation of cellulose surfaces

Cellulose-gelatin interactions were investigated by using gold-coated sensors in SPR and QCM-D experiments. The sensors (SPR gold chips or QCM crystals) were first cleaned with UV/ozone treatment for 15 min followed by spin coating with 0.1 wt.% polystyrene in toluene (4000 rpm, 60 s). Prepared polystyrene-coated sensors were then dried in an oven at 60 °C for 10 min to ensure a uniform hydrophobic layer suitable for trimethylsilyl cellulose (TMSC) deposition. TMSC was deposited on the polystyrene-coated sensors by using the Langmuir–Schaeffer (LS) lifting deposition technique as described by Tammelin et al. [32]. The TMSC layer was then converted to cellulose via desilylation with hydrochloric acid vapor as described elsewhere [33]. The crystallinity degree, thickness, and roughness of the LS-cellulose films prepared in the same manner have previously been observed to be 54%, 17.8 nm, and 0.5 nm, respectively [34]. Before QCM-D and SPR experiments the cellulose films were allowed to stabilize overnight in the appropriate buffer solution.

2.3. Adsorption experiments using cellulose sensors

Prior to QCM-D and SPR adsorption experiments, gelatin was dissolved in Milli-Q water and dialyzed using a 10–12 kDa mesh membrane tube (SpectraPor, Spectrumlabs) and freeze-dried. Isoelectric point of gelatin was measured using zeta-potential analyzer (Malvern Zetasizer Nano ZS device, Malvern Instruments, Malvern, UK). Dialyzed gelatin was dissolved in 10 mM acetate, phosphate and bicarbonate buffers at pH 4, 5.8 and 10, respectively at 45 °C for 30 min to yield 0.1 mg/mL concentration. Afterwards, gelatin solution was filtered using 0.45 µm filters and degassed. Both QCM-D and SPR experiments were performed at a constant flow rate of 100 µL/min and the temperature was maintained at 21 °C until adsorption plateau was reached. Thereafter, rinsing with polymer-free buffer solution was applied to ascertain the irreversible binding of gelatin to cellulose surfaces pre-adsorbed on the (QCM/SPR) sensors. Finally, the sensors were washed with Milli-Q water and stored in desiccator until further investigation. Each set of experiments was performed at least two times.

2.4. Adsorbed mass by using quartz crystal microbalance and surface plasmon resonance

Gelatin adsorption onto cellulose and properties of adsorbed gelatin layer were investigated by using quartz crystal microbalance with dissipation (QCM-D) monitoring (E4 instrument, Q-Sense AB, Sweden) and surface plasmon resonance (SPR) unit

Download English Version:

<https://daneshyari.com/en/article/5209786>

Download Persian Version:

<https://daneshyari.com/article/5209786>

[Daneshyari.com](https://daneshyari.com)